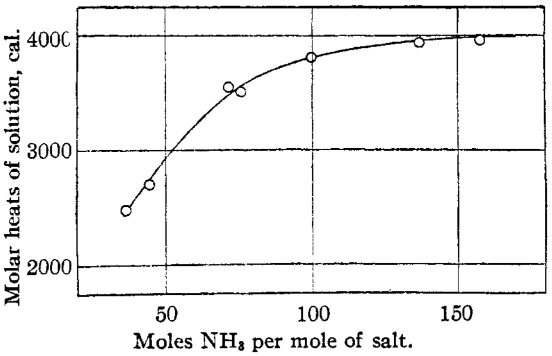

Fig. 2.—Molar heats of solution of sodium nitrate.

concentrated solutions could not be examined because of the low solubility of this salt. The heat of solution of methanol in liquid ammonia lies between that of water (3224 cal.)[6] and ethanol (1100 cal.),[4] as would be expected. Examination of Table II shows that as the number of carbon atoms in the normal alcohols increases, the molar heat of solution decreases.

TABLE I

MOLAR HEATS OF SOLUTION OF AMMONIUM AND SODIUM SALTS AT −33.4°

Sample, g.	Moles NH_3 per mole of salt	Molar heat effect, cal.
	Ammonium Iodide	
4.269	56.1	20860
2.764	74.0	16700
2.145	98.6	16750
1.606	129.5	14900
0.680	372.2	13450
.451	562.1	13350
.349	726.5	13000
	Sodium Iodide	
2.375	107.6	18850
2.209	116.1	17360
1.587	162.9	15700
1.290	200.9	15250
0.553	472.4	14000
.357	732.9	13900
	Sodium Nitrate	
0.942	157.5	3960
1.084	136.9	3930
1.485	99.7	3810
1.959	75.6	3510
2.068	71.3	3550
3.333	44.5	2700
4.024	36.7	2480
	Sodium Chloride	
0.589	174.5	1460
.518	197.9	1480

TABLE II

MOLAR HEATS OF SOLUTION OF SOME ALCOHOLS AT −33.4°

Alcohol	Sample, g.	Moles NH_3 per mole alcohol	Molar heat effect, cal.
Methanol	1.044	53.0	1960
Methanol	1.602	34.8	1996
n-Propanol	1.582	66.5	655
n-Butanol	1.387	93.0	− 100
Benzyl	2.214	85.6	600
Furfuryl	2.242	76.7	580

Summary

The molar heats of solution of ammonium iodide and sodium iodide have been measured over a wide range of concentration and found to have a negative heat of dilution.

Heats of solution of sodium nitrate and sodium chloride, as well as those of a few alcohols, are reported.

[6] C. A. Kraus and F. C. Schmidt, THIS JOURNAL, **56**, 2297 (1934).

SCHENECTADY, N. Y. RECEIVED AUGUST 6, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Complex Ions. II. The Stability and Activity Coefficients of the Silver-Ammonia Ion[1]

BY PAUL F. DERR, RUTH M. STOCKDALE AND W. C. VOSBURGH

Randall and Halford[2] have measured the solubility of silver chloride in ammonia solutions and have shown their results to be in good accord with those of previous workers. They have calculated the activity coefficients of the complex salt $Ag(NH_3)_2Cl$ and the dissociation constant of the complex ion. The activity coefficients are smaller than the corresponding activity coefficients of simple uni-univalent salts. Whether they are true activity coefficients or stoichiometric ones applying only to this reaction is not shown. The latter is the more probable, since the true activity coefficients of the complex ion would not be expected to differ much from those of the silver ion or other univalent ions.

In connection with another investigation it was

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[1] Part of a thesis submitted by Paul F. Derr in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

[2] Randall and Halford, THIS JOURNAL, **52**, 178 (1930). References to previous work are given by Randall and Halford.

important to know whether or not the activity coefficient of a complex ion may be assumed approximately equal to the activity coefficient of a simple ion of the same valence type. The dissociation constant of the silver-ammonia ion was also of interest, and some measurements of the solubility of silver iodate in ammonia solutions which were undertaken to check the constant have answered the question about the activity coefficients.

The dissociation constant found agrees well with the value of Randall and Halford, but the activity coefficients of the silver-ammonia ion were found to be practically equal to those of the silver ion. Data for the solubility of silver chloride in ammonia solutions containing potassium nitrate or potassium chloride gave additional evidence that the activity coefficients of Randall and Halford are not the true ones for the complex salt.

Materials.—Silver iodate was prepared by the slow addition of one liter of 1 *M* silver nitrate solution and two liters of 0.5 *M* potassium iodate solution to 500 ml. of water in the dark with continuous stirring. After digestion on a hot-plate for twenty-four hours the precipitate was well washed and dried in air. Analysis of two preparations after drying at 110° gave good agreement with the theoretical composition.

A 0.5 *M* stock solution of ammonia was prepared by dilution of a concentrated solution that had been shown by analysis to contain a negligible amount of carbonate. The solution was preserved in a bottle lined with Vulcalock cement[3] and was protected from atmospheric carbon dioxide.

A 2.00 *M* ammonium nitrate solution was prepared by neutralization of standardized 8 *M* nitric acid solution (shown to be free from nitrite) with standard ammonia solution and dilution.

Potassium nitrate of reagent grade was recrystallized and dried for several hours at 110°.

Sodium hydroxide solution, 0.1 *N*, was standardized against potassium acid phthalate from the National Bureau of Standards, or an equivalent recrystallized preparation. It was preserved as described for the ammonia solution. Hydrochloric acid solution, 0.1 *N*, was standardized against the sodium hydroxide solution. Sodium thiosulfate solution, 0.1 *N*, was standardized against recrystallized potassium iodate at least every two weeks. The thiosulfate solution was preserved with sodium furoate.[4] When 0.01 *N* thiosulfate was needed it was prepared fresh each day by careful dilution of the 0.1 *N* solution.

The Solubility of Silver Iodate in Potassium Nitrate Solutions.—Kolthoff and Lingane[5] and Li and Lo[6] have measured the solubility of silver iodate in potassium nitrate solutions. Some additional measurements were made before the results of the latter authors were published in order to check the silver iodate preparations and the technique, and to provide more data in the region of ionic strength of particular interest in this investigation.

Potassium nitrate solutions were made by careful weighing of the pure salt, dissolving and making up to known volume. These solutions were saturated with silver iodate in Pyrex flasks immersed in a water-bath at 25° in a weak, diffused daylight or artificial light. Efficient stirring for two hours was shown to be sufficient for saturation. Samples were taken after three to four hours and again two or more hours later to test the constancy of the concentration.

The samples were taken by means of a 200-ml. pipet to which was attached a filter either of Pyrex glass wool or Pyrex fritted glass. The samples were weighed so that the molality could be calculated, and the iodate content was determined by titration with 0.01 *N* thiosulfate solution.

It was assumed that the silver ion concentration was equal to the iodate ion concentration as determined by analysis. Kolthoff and Lingane[5] found that it was necessary to coat their bottles with paraffin to prevent exchange adsorption of silver ions with the glass, and they determined both silver and iodate. In this investigation coating the flasks with paraffin or Vulcalock cement[3] made no difference in the results, nor did a considerable increase in artificial illumination. If stirring of the saturated solutions with the excess solid was continued after the usual saturation period, a slow increase in the iodate concentration sometimes took place, but not always. The increase seemed to bear no relation to the conditions named above, and its cause was not determined.

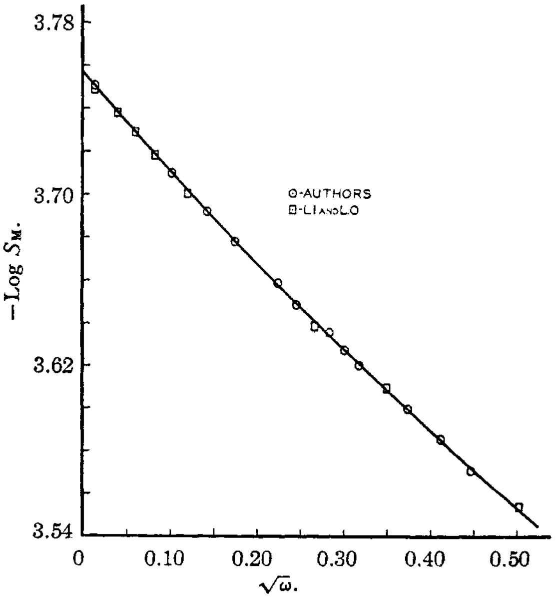

Fig. 1.—The solubility of silver iodate in potassium nitrate solutions: □, Li and Lo; O, this investigation.

The results are shown in Fig. 1 together with some of the values of Li and Lo. The latter are so near like the

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[3] This was obtained from the B. F. Goodrich Co.; see Soule, *Ind. Eng. Chem., Anal. Ed.*, **1**, 109 (1929).

[4] Platow, *Chemist Analyst*, **28**, 30 (1939).

[5] Kolthoff and Lingane, *J. Phys. Chem.*, **42**, 133 (1938).

[6] Li and Lo, THIS JOURNAL, **63**, 394 (1941).

results of Kolthoff and Lingane that it was impossible to represent both. The line represents the equation

$$-\log S_M = -\log S_M^0 - [0.5056\ \sqrt{\omega}/(1 + \sqrt{\omega}) + 0.150\ \omega] \quad (1)$$

in which S_M is the solubility in moles per liter and S_M^0 that at zero ionic strength. The brackets enclose an expression for the mean activity coefficient in terms of ω, the ionic strength on the concentration basis. Solubilities calculated from this equation differ from the observed values by a maximum of 4 or an average of ±1.7 parts in 1000. The solubility at zero ionic strength is 1.746×10^{-4} mole per liter as compared with 1.744 found by Kolthoff and Lingane and 1.748 by Li and Lo. The solubility in terms of molality is given by the equations

$$\log S_m = \log S_M^0 - \log \gamma \quad (2)$$

$$-\log \gamma = 0.5056\ \sqrt{\mu}/(1 + \sqrt{\mu}) + 0.160\ \mu \quad (3)$$

in which S^0 is $1.754 \times 10^{-4}\ m$. The corresponding activity solubility product is 3.076×10^{-8}.

The Solubility of Silver Iodate in Ammonia Solutions.—The solubility of silver iodate in ammonia solutions was determined essentially as described for the potassium nitrate solutions, with an ammonia solution substituted for the salt solution. In some of the experiments ammonium nitrate or potassium nitrate was included in the solution. Samples were taken by forcing the solution through the filter and into the pipet by air pressure to avoid loss of ammonia. The samples were delivered into an excess of 0.1 N hydrochloric acid solution and the excess titrated with 0.1 N sodium hydroxide solution with methyl red as the indicator. Then the iodate content of the samples was determined by titration with 0.1 N thiosulfate solution. This procedure was shown to give as good results as the use of separate samples for the two determinations.

TABLE I

SOLUBILITY OF SILVER IODATE IN AMMONIA SOLUTIONS AT 25°

NH_3, total, m	IO_3^-, $m \times 10^3$	NH_4NO_3, m	Density	$\mu \times 10^2$	$K \times 10^8$
0.01241	3.665	....	0.997	0.398	6.07
.01267	3.752	....	.997	.406	5.99
.01845	5.488	....	.997	.587	6.13
.02481	7.430	....	.998	.788	6.13
.03085	9.358	....	.997	.986	5.92
.06180	19.01	....	1.003	1.974	6.11
.03677	11.45	0.0099	0.999	2.14	6.17
.03599	11.25	.0102	.998	2.15	6.05
.01277	4.002	.0200	.997	2.40	6.18
.1028	32.23	....	1.003	3.32	6.04
.1249	39.32	....	1.005	4.04	6.18
.03619	11.48	.0403[a]	1.001	5.24	5.99
.01403	4.515	.0503	0.998	5.48	6.17
.1847	59.37	....	1.009	6.07	6.05
.03615	11.87	.0694	1.001	8.13	6.01
.2487	81.25	....	1.014	8.28	5.97
.01245	4.049	.0998[a]	1.003	10.42	5.83
.01347	4.544	.1301	1.001	13.46	6.02
.03626	12.20	.1241	1.002	13.63	6.03
.03628	12.12	.1424[a]	1.007	15.51	5.94

[a] In these experiments potassium nitrate was substituted for ammonium nitrate.

The results are given in Table I. From the iodate ion molality in the second column and the solubility product of silver iodate, 3.076×10^{-8}, together with activity coefficients from Equation 3, the silver ion molality was calculated. Subtracting this from the total silver molality (which was assumed equal to the iodate ion molality) gave the molality of the complex ion. The complex ion was assumed to be $Ag(NH_3)_2^+$. Twice its molality subtracted from the total ammonia molality gave the total free ammonia. This was then corrected by the subtraction of the molality of ammonium (or hydroxide) ion formed by reaction with water. This molality was calculated from the ionization constant of ammonia, for which the value[7] 1.75×10^{-5} was used, with activity coefficients calculated from the Debye–Hückel equation. The correction was small enough so that the possible errors in the calculation were unimportant. When ammonium nitrate was added, this correction was negligible. From the corrected free-ammonia molality, and the silver and complex ion molality the instability constants in the last column of Table I were calculated by the equation

$$[Ag^+][NH_3]^2 = K[Ag(NH_3)_2^+]$$

in which brackets indicate molality. The activity coefficients for the two ions of the same valence type were assumed to cancel, and the activity of ammonia was considered equal to its molality.[8] The absence of any regularity in the variation of K lends support to these assumptions. The average value of K is 6.05×10^{-8}, with an average deviation of $\pm 0.07 \times 10^{-8}$. This value for K is in good agreement with 6.07×10^{-8} found by Randall and Halford.[2] If the value of the solubility product of silver chloride given by MacInnes[9] is combined with the solubility data of Randall and Halford, the value 6.03×10^{-8} is obtained for K. Bjerrum[10] by means of glass electrode measurements in ammoniacal silver nitrate solutions obtained 5.9×10^{-8} for K at 25°. This value is subject to larger

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(7) (a) Everett and Wynne-Jones, *Proc. Roy. Soc.* (London), **A169**, 190 (1939); (b) Owen, THIS JOURNAL, **56**, 2785 (1934).

(8) (a) Ref. 2, p. 192; (b) Scheffer and de Wijs, *Rec. trav. chim.*, **44**, 655 (1925).

(9) MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, N. Y., 1939, p. 318.

(10) Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941, p. 130.

error than the value from this investigation, and the agreement is satisfactory.

Bjerrum presents evidence for the existence of a monamine ion, $AgNH_3^+$. In the present investigation conditions were unfavorable for the existence of this ion, since the silver ion concentration was always small and the free ammonia concentration much larger. Calculation by means of Bjerrum's instability constant, 4.8×10^{-4}, gives amounts of the monammine that would be appreciable in the more dilute solutions, but negligible in the more concentrated. If the monammine is as important as the calculation indicates in the more dilute solutions, its neglect should lead to a regular variation in K. That such a variation does not occur may be the result of a compensating error, perhaps in the assumption concerning the activity coefficients, or it may be that Bjerrum's constant is too small. It is probable that the latter is true, because Bjerrum has pointed out that there is considerable uncertainty in the calculation of this particular constant.

The Solubility of Silver Chloride in Ammonia Solutions.—The activity coefficients found by Randall and Halford for silver ammonia chloride decrease faster with increasing molality than values calculated from the Debye–Hückel limiting law, while the activity coefficients of silver nitrate as given by MacInnes[9] (p. 165) decrease a little more slowly. These facts do not seem to accord well with the assumption of equality of the activity coefficients of the silver and silver-ammonia ions. They can be explained by the assumption of the presence of a second complex compound in ammoniacal silver chloride solutions, which is not present in ammoniacal silver iodate solutions. The difference between these two solutions would be understandable if chloride ion is a constituent of the compound. To test this explanation some determinations were made of the solubility of silver chloride in dilute ammonia solutions with addition of potassium nitrate or chloride to increase the ionic strength.

Silver chloride was prepared by slow precipitation from silver nitrate and hydrochloric acid, and was digested with hot water, washed thoroughly, and dried at 110°. Exposure to daylight was avoided by working in a dark-room. Ammonia solutions, to most of which had been added some recrystallized potassium nitrate or chloride, were saturated with silver chloride and samples taken by the procedure described above. The ammonia was determined, and the solutions containing the samples were then acidified with hydrochloric acid and the precipitated silver chloride was digested and weighed.

TABLE II

SOLUBILITY OF SILVER CHLORIDE IN AMMONIA SOLUTIONS

NH_3, total, m	Ag, total, m	KNO_3, m	$\mu^{1/2}$	$-\log(K')^{1/2}$
0.08905	0.004538	....	0.077	1.238
.08731	.005209	0.0534	.245	1.161
.08232	.005203	.1057	.335	1.131
.08961	.005948	.1638	.414	1.106
.08821	.006442	.335	.585	1.058
.08735	.006768	.604	.783	1.026
2.013	.1511	....	.398	1.052
0.3707	.01724	.0106[a]	.175	1.183
.3495	.01143	.0312[a]	.214	1.166
.2988	.002958	.3222[a]	.573	0.978

[a] Potassium chloride instead of nitrate.

The results are given in Fig. 2 and Table II.

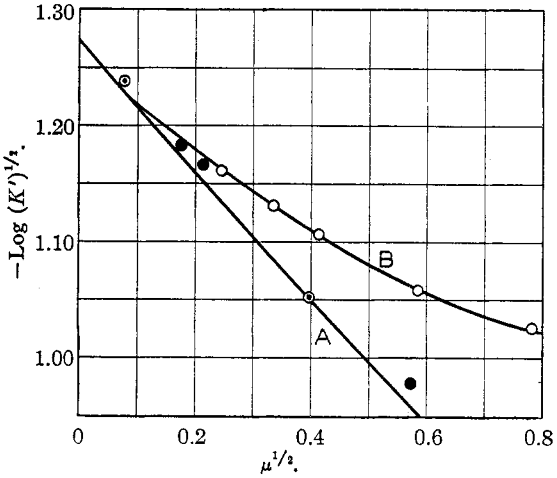

Fig. 2.—Variation of the classical equilibrium constant, K', of the reaction $AgCl(s) + 2NH_3 \rightleftarrows Ag(NH_3)_2^+ + Cl^-$ with ionic strength: ◉, silver chloride in ammonia solution with no added electrolytes; ○, nearly constant total ammonia concentration and ionic strength varied by addition of potassium nitrate; ●, same with potassium chloride instead of nitrate. Curve A is the curve of Randall and Halford.

For Fig. 2 the reaction on dissolving the silver chloride was assumed to be

$$AgCl(s) + 2NH_3 \rightleftarrows Ag(NH_3)_2^+ + Cl^-$$

and K' is defined by

$$[Ag(NH_3)_2^+][Cl^-] = [NH_3]^2K'$$

Curve A is that of Randall and Halford, with two experimental points of this investigation lying practically on it. In these two experiments no potassium nitrate or chloride was added to the ammonia solution. With the exception of the more concentrated of these two solutions, and the three to which chloride was added, the solutions of the experiments of Fig. 2 were all between 0.082 and 0.090 M in total ammonia and the ionic strength was varied by the addition of potassium nitrate. The values of $-\log (K')^{1/2}$ for these experiments all lie on Curve B. It is evident that K' is not a function of ionic strength alone, and the activity coefficients calculated from the experiments of Randall and Halford cannot be true ones for the complex salt. When a fairly dilute ammonia solution was used and potassium chloride added, K' falls between the two curves, showing that the value of K' depends on the chloride ion concentration. Extrapolation to zero ionic strength should eliminate the effect of the chloride ion, and the constant of Randall and Halford should be without error from this source.

Summary

Previous measurements of the solubility of silver iodate in solutions of potassium nitrate have been checked.

The solubility of silver iodate in ammonia solutions has been determined. The instability constant of the diammine-silver ion calculated from the solubility data agreed with the best of the previous results.

Assumption of equality of the activity coefficients of the silver and diammine-silver ions gave consistent results.

Measurements of the solubility of silver chloride in ammonia solutions containing potassium nitrate or potassium chloride showed that the solubility is dependent on the chloride ion concentration as well as on the ammonia concentration and the ionic strength.

DURHAM, NORTH CAROLINA RECEIVED JULY 28, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

A Study of the Products Obtained by the Reducing Action of Metals upon Salts in Liquid Ammonia Solution. VI. The Reduction of Nickel Salts

BY WAYLAND M. BURGESS AND JOHN W. EASTES[1]

Introduction

The reduction of metal salts by solutions of sodium (or potassium or calcium) in liquid ammonia forms first the free metal in a finely divided state. This may act as an efficient catalyst for the reaction between sodium and ammonia or it may take part in other reactions such as the formation of an intermetallic compound with sodium.[2–6]

With nickel salts that furnish a nickel cation, reactive metallic nickel has been prepared. Calcium as a reducing agent gave the most active form of precipitated metal. No intermetallic compound was formed. When salts containing nickel in the anion were reduced, free nickel was not a product. Since different results were obtained with the two types of nickel compounds, their reduction will be presented in two sections. The present article deals with the reduction of nickel cations.

Preparation of Nickel Salts.—Nickel salts (chloride, bromide, iodide, thiocyanide, acetate, cyanide) with ammonia of crystallization were used in this work. Nickel hexammine acetate and nickel triammine cyanide, were formed by washing the hydrated salt with liquid ammonia, then removing the excess ammonia by evacuation at about 20 mm. of mercury. No reference has been found in the literature to these particular ammines.

Nickel hexammine acetate is of a light violet color, stable in dry ammonia or dry air, but quite unstable in moist air.

Anal. Calcd. for $Ni(C_2H_3O_2)_2 \cdot 6NH_3$: Ni, 21.04; NH_3, 36.65. Found: Ni, 21.3; NH_3, 36.4.

Nickel triammine cyanide is also of a light violet color but is stable in ordinary air.

Anal. Calcd. for $Ni(CN)_2 \cdot 3NH_3$: Ni, 36.27; CN, 32.16; NH_3, 31.57. Found: Ni, 36.4; CN, 32.3; NH_3, 32.9.

Reduction Reactions Using Potassium.—The apparatus employed was essentially the same as described in previous articles.[2,5]

Two reactions occurred concurrently as may be represented by equations (1) and (2).

$$2K + NiBr_2 \longrightarrow 2KBr + Ni \qquad (1)$$

$$2K + 2NH_3 \longrightarrow 2KNH_2 + H_2 \qquad (2)$$

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by John W. Eastes in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1936.

(2) Burgess and Rose, THIS JOURNAL, **51**, 2127 (1929).

(3) Burgess and Smoker, *ibid.*, **52**, 3573 (1930).

(4) Burgess and Smoker, *Chem. Rev.*, **8**, 265 (1931).

(5) Burgess and Holden, THIS JOURNAL, **59**, 459 (1937).

(6) Burgess and Holden, *ibid.*, **59**, 462 (1937).